"Green" High-Temperature Polymers

PMR-15 is a processable, high-temperature polymer developed at the NASA Lewis Research Center in the 1970's principally for aeropropulsion applications. Use of fiber-reinforced polymer matrix composites in these applications can lead to substantial weight savings, thereby leading to improved fuel economy, increased passenger and payload capacity, and better maneuverability. PMR-15 is used fairly extensively in military and commercial aircraft engines components seeing service temperatures as high as 500 °F (260 °C), such as the outer bypass duct for the F-404 engine. The current world-wide market for PMR-15 materials (resins, adhesives, and composites) is on the order of \$6 to 10 million annually.

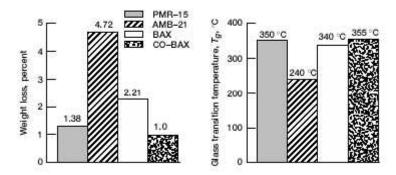
PMR-15 is prepared with a monomer, methylenedianiline (MDA), which is a known animal and suspect human carcinogen. The Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) heavily regulate the use of MDA in the workplace and require certain engineering controls be used whenever MDA-containing materials (e.g., PMR-15) are being handled and processed. Implementation of these safety measures for the handling and disposal of PMR-15 materials costs the aircraft engine manufacturing industry millions of dollars annually.

$$NH_2$$
 CH_2 CH_2 CH_2 CH_2 NH_2
 $MDA ext{ (used in PMR-15)}$ BAX
 H_2N CH_2 CH_2 NH_2
 CO CH_2 NH_2
 CO CH_3 CH_2 NH_2
 CO CH_3 CH_3 CH_3 CH_4 CH_5 CH_5

Some candidate diamines for replacing MDA (top left) in PMR-15.

Under the Advanced Subsonic Technology (AST) Program, researchers at NASA Lewis, General Electric, DuPont, Maverick Composites, and St. Norbert College have been working to develop and identify replacements for PMR-15 that do not rely upon the use of carcinogenic or mutagenic starting materials. This effort involves toxicological screening (Ames' testing) of new monomers as well as an evaluation of the properties and high-temperature performance of polymers and composites prepared with these materials. A number of diamines have been screened for use in PMR-15 replacements. Three diamines, BAX, CO-BAX, and BAPP (see the preceding chemical illustration), passed the Ames' testing. Graphite-reinforced composites prepared with polyimides containing these diamines were evaluated against a PMR-15 control in terms of their high-temperature

stability (weight loss after 125 hr in air at 316 °C and 5-atm pressure) and glass-transition temperature (an indication of high-temperature mechanical performance). Of these three materials systems, both the BAX and CO-BAX composites had stabilities and glass-transition temperatures comparable to those of PMR-15 (see the graphs). Further evaluation of the processability of these materials as well as their long-term stability and mechanical performance at 288 °C (550 °F) is in progress.



Comparison of the glass-transition temperature and thermal-oxidative stability of graphite-reinforced composites prepared with non-MDA PMR-15 replacements. Left: Weight loss after 125 hr in air at 316 °C and 5 atm. Right: Glass-transition temperature.

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